Effect of grain-scale pressure variations on garnet growth: A numerical approach

Journal Article**Author(s):**

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Publication date:

2017-01

Permanent link:

<https://doi.org/10.3929/ethz-a-010744283>

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Originally published in:

Journal of Metamorphic Geology 35(1), <https://doi.org/10.1111/jmg.12213>

Funding acknowledgement:

335577 - Interplay between metamorphism and deformation in the Earth's lithosphere (EC)

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9 **Garnet growth under pressure variation**

ABSTRACT

Grain-scale pressure variations have recently been investigated due to its significant effect on the observed microstructures and chemical redistribution in metamorphic rocks. In this study, we investigate the impact of grain-scale pressure variation on a growing grain, specifically on garnet. We model prograde garnet growth at fluid saturated conditions and sufficiently low temperature ($<650^{\circ}\text{C}$) to avoid modification of the inner part of the grain by diffusion. The method uses the Perple_X computer program package combined with Matlab® scripts allowing for a heterogeneous fluid pressure distribution around the growing grain. It is shown that the pressure variation around the grain may result in an asymmetric chemical zonation. Motivated by the result, we apply the model to selected published prograde paths to evaluate the magnitude of the pressure variation that is necessary for the development of the asymmetric zoning preserved in the samples. The magnitude of such a pressure gradient in the selected samples corresponds up to 1 kbar. Finally, it is demonstrated that the modelling of asymmetric chemical zoning in garnet under a pressure gradient may improve the precision of thermobarometric constraints. The numerical model evaluates the effect of the pressure gradient on a growing grain and thus can serve as a benchmark tool in future development of fully coupled models involving rock deformation and mineral reactions.

Keywords: Asymmetric chemical zoning, garnet, pressure variation, prograde metamorphism, equilibrium thermodynamics.

34 INTRODUCTION

35 The concept of equilibrium under a pressure gradient has been gradually adopted and
36 emphasized due to its significance on the preserved microstructure and compositional
37 variations in rocks (Tajčmanová *et al.*, 2014; 2015). Pressure variation has been
38 directly measured (e.g. Nasdala *et al.*, 2005; Chen *et al.*, 2015), numerically modeled
39 at different scales (Mancktelow, 1993; Petrini & Podladchikov, 2000; Moulas *et al.*,
40 2014; Dabrowski *et al.*, 2015) and systematically investigated on its significance for
41 the preserved chemical zonation (Tajčmanová *et al.*, 2014, 2015; Moulas *et al.*, 2015;
42 Zhong *et al.*, 2015). One of the main causes of grain-scale pressure variation is
43 deformation due to heterogeneous viscosity distribution (Schmid & Podladchikov
44 2003; Moulas *et al.*, 2014; Tajčmanová *et al.*, 2015). Another typical example is a
45 radial pressure variation caused by the expansion of a stressed inclusion surrounded
46 by a relaxed host matrix (Zhang, 1998; Tajčmanová *et al.*, 2014; Dabrowski *et al.*,
47 2015; Angel *et al.*, 2015). Dabrowski *et al.* (2015) provided an analytical solution to
48 estimate the time scale of viscous pressure relaxation in an inclusion–host system and
49 concluded that it may last up to a million year. Moreover, Tajčmanová *et al.* (2014)
50 documented the effect of grain scale pressure variation on the preserved chemical
51 zonation in plagioclase at high temperature where diffusion is expected to be
52 significant.

53 Based on theoretical and experimental studies, fluid pressure has been confirmed to
54 exert the first order control on common metamorphic reactions and mineral growth
55 (Gibbs, 1876; Dahlen, 1992; Llana–Funez *et al.*, 2012, Hobbs & Ord, 2015).
56 Understanding the development of prograde chemical zoning of a perfectly
57 fractionating grain in the presence of pressure gradients in fluid saturated systems is
58 an important step for further quantitative models of dynamic fluid pressure evolution
59 and mineral reactions during prograde metamorphism. The results of such an
60 idealized fractionating approach could then be used as a benchmark in the
61 development of predictive dynamic models. Therefore, the aim here is to investigate
62 the growth of a mineral along a fluid saturated prograde P – T path under a grain-scale

63 fluid pressure gradient.

64 In the lower crust, the fluid pressure (P_f) is conventionally considered to be equal to
 65 the lithostatic pressure (P_l) because fluid is sealed in low porosity and permeability
 66 metamorphic rocks (Spear, 1993; Winter, 2010). However, during devolatilization
 67 reactions the fluid pressure can deviate from lithostatic at the reaction front (Connolly,
 68 2010; Connolly & Podladchikov, 2012). In Fig. 1a (modified after Connolly, 2010),
 69 such a fluid pressure behavior is depicted. In the area above and below the reaction
 70 region, rocks are considered to be compact and the fluid pressure equals to the
 71 lithostatic pressure. Within the reaction region, the porosity and permeability are
 72 elevated which allows the fluid pressure to follow the hydrostatic gradient (the blue
 73 line in Fig. 1a). The hydrostatic gradient is generally lower than the lithostatic
 74 pressure gradient because fluids are less dense than rocks (Connolly, 2010). The
 75 inequality between the macroscopic fluid pressure and the lithostatic pressure for a
 76 continuum in the reaction region illustrated in Fig. 1a has consequences for the
 77 microscopic pressure variation at the grain-scale. In Fig. 1b, a schematic thin-section
 78 is drawn for a situation at a certain depth corresponding to the reaction region
 79 (indicated with the horizontal dash line). Neglecting tectonic deformation, the
 80 pressure at the grain-grain interface (black spot in Fig. 1b) has to be equal to the
 81 lithostatic pressure (black spot in Fig. 1a) in order to support the weight of the
 82 overlying rocks. In other words, this situation at the fluid-saturated grain-grain
 83 interface is due to the necessity to maintain force balance across the interface so that
 84 the rock does not collapse (Robin, 1978; Rutter, 1983; Gratier, 2013). However, if
 85 fluid flow is sufficiently fast to equalize fluid pressure, the pressure in pores (red spot
 86 in Fig. 1b) follows the hydrostatic fluid pressure gradient (the blue line in Fig. 1a).
 87 Therefore, in the case of a metamorphic rock in which flow is sufficiently fast to
 88 establish a hydrostatic pressure gradient, fluid pressure is not equal to the lithostatic
 89 pressure in some parts of the reaction region. This results in a grain-scale variation
 90 between the fluid pressure in open pores (P_f = hydrostatic) and the fluid pressure at
 91 grain-grain interface (P_f = lithostatic). Such a fluid pressure variation will be

92 maintained on the compaction time scale due to force balance. The above conceptual
93 descriptions are in agreement with studies on pressure solution. It has been found that
94 a thin (hundred *nm* scale) porous layer between grain–grain interface can remain fluid
95 saturated during metamorphism (Gratier *et al.*, 2013). The pressure difference
96 between the fluid saturated thin layer and open pores has been recognized as the
97 driving force responsible for dissolution–precipitation creep (Robin, 1978; Passchier
98 & Trouw, 1998 p. 26; Bernabe & Evans, 2007).

99 Here, we chose garnet as a representative mineral to investigate the effect of grain–
100 scale pressure variation on prograde zoning and growth of a metamorphic mineral
101 because it has been extensively recognized as a fractionated phase to determine the
102 pressure–temperature (P – T) history in metamorphic rocks (e.g. Tracy & Robinson,
103 1976; Cygan & Lasaga, 1982; Spear *et al.*, 1991). We develop a numerical model
104 based on the Perple_X computer program package (Connolly, 2009) described in the
105 following chapter. Matlab® codes in combination with the Perple_X equilibrium
106 thermodynamic solver are used to allow for pressure variation around the
107 fractionating garnet during a prograde path up to 650 °C. We quantify the magnitude
108 of pressure variations from equilibrium thermodynamic calculations and investigate
109 the effect on garnet growth and chemical zoning. The results show that the local
110 deviations from isobaric conditions can be responsible for the development of
111 asymmetric chemical zoning.

112

113 **MODEL DESCRIPTION**

114 The model of Vrijmoed & Hacker (2014) is extended here to include pressure
115 variation as an additional parameter. The model is separated into two parts: (1) a
116 forward model part to calculate the chemical profile for a given prograde P – T path at
117 a fixed magnitude of pressure variation, and (2) an optimization part to determine the
118 best fit P – T path and the magnitude of pressure variation for a given rock. As the
119 prograde P – T path is placed at relatively low temperature condition (<650°C) no

chemical diffusion is considered within garnet. Based on experimental and numerical works, diffusion of chemical components along fluid saturated grain boundaries around a growing mineral can be as fast as in bulk water or ca. one or two orders of magnitude slower (Dysthe *et al.*, 2002; Alcantar *et al.*, 2003; Gratier *et al.*, 2013). Therefore, in this model, we consider that the chemical homogenization along grain boundaries and/or interconnected porosity in the matrix (Fig. 1b) is achieved rapidly.

126

127 **Garnet growth along a P – T path – A forward model**

The pressure variation around a growing garnet is simplified as a sinusoidal function shown in (Fig. 2a). At each point along the P – T path, the garnet rim is discretized into cells (Fig. 2b) in which Gibbs free energy minimization using Perple_X (Connolly, 2009) is performed to retrieve local garnet composition and modal proportion from a common effective bulk composition, at constant temperature, and different pressure within each cell.

The garnet equilibrium volume calculated in individual cells is converted to 2D sectorial area and attached to the surface of the garnet rim (Fig. 2b, and Appendix S1). Following the model setup, the garnet volume difference among cells is a result of the local fluid pressure variation. The composition calculated for each cell is scaled based on its weight percentage, summed up, and fractionated from the bulk composition for the calculation of the next step. Afterwards the rock moves to the next P – T point with fixed P – T increment along the path using the fractionated bulk composition for all the cells until the final P – T conditions are reached (Fig. 2c). To investigate the first order effect of the pressure variation, its magnitude is assumed to be constant along the P – T path. More detailed description of the numerical model is provided in Appendix S1 and the effect of P – T increment along the P – T path is provided in Discussions and Implications. A benchmark of the forward model is given in Appendix S2.

The test example in Fig. 2b is computed using a pelitic bulk composition and a typical prograde P – T path from Russo *et al.* (2006) under 0.5 kbar maximum pressure

148 variation around the garnet. The significant asymmetry of the garnet shape and
 149 chemical zoning pattern demonstrate the potential importance of grain-scale pressure
 150 variation on garnet growth (see the development of asymmetry in Fig. 2b). The
 151 method to estimate the magnitude of maximum pressure variation is described in the
 152 following section.

153

154 **Optimization of the P – T path and pressure variation ($Pvar$)**

155 An inverse modelling technique based on a brute-force search method (Vrijmoed &
 156 Hacker, 2014) is used to obtain the best fit P – T – $Pvar$ conditions to the measured
 157 natural garnet zoning profiles. The peak P – T conditions can be constrained with phase
 158 equilibria modelling and geothermobarometry using as a first guess the averaged
 159 garnet rim composition in order to estimate the peak P – T conditions for further garnet
 160 growth modelling. The starting P – T conditions and the pressure variation are
 161 constrained and meshed on 3–D coordinates for a fixed P – T increment (Fig. 3a).
 162 These three independent variables, i.e. the starting pressure, starting temperature and
 163 the amplitude of pressure variation, are independently varied to find the best fit P – T –
 164 $Pvar$ conditions (Fig. 3a). The garnet zoning profile is first calculated from one of the
 165 P – T – $Pvar$ conditions using the forward model described earlier. The zoning profile is
 166 subsequently compared to the measured profile to quantify the residual (Fig. 3b). For
 167 this purpose, the garnet modal volume is normalized to the grain size of the measured
 168 garnet profile. The individual residual for each end-member component can be
 169 quantified. The method to quantify the residual is described in Vrijmoed & Hacker
 170 (2014) and illustrated in Fig. 3b. After evaluating the residual for individual end
 171 member components, the total residual is summed using the individual residual from
 172 all the four end members. Subsequently, the starting P – T – $Pvar$ point is moved over to
 173 the next grid and the same procedure is repeated (Fig. 3a).

174

175 **MAGNITUDE OF THE PRESSURE VARIATION FOR ASYMMETRIC** 176 **GARNETS**

177 Three representative asymmetrically zoned garnets have been collected from the
 178 literature to investigate the magnitude of the pressure variation.

179

180 **Description of selected samples**

181 The first sample, SR123, is a Ca-poor micaschist in Aspromonte Massif (southern
 182 Calabria, Italy; Russo *et al.*, 2006). The second sample, OF2512, is an ultra-high
 183 pressure rock (Groppo *et al.*, 2009) collected from Lago di Cignana (Western Alps
 184 containing coesite-eclogite facies. The third sample, TRE 1, is a blueschist from Ile
 185 de Groix (Armorican Massif, France; Ballevre *et al.*, 2003). Bulk compositions of
 186 these samples are provided in Figure 4 together with isochemical phase-diagram
 187 sections. The phase-diagram sections are calculated with the Gibbs energy
 188 minimization Perple_X software package (Connolly, 2009) using the thermodynamic
 189 database of Holland & Powell (1998, as revised in 2003). The solid solution models
 190 used in the calculation are indicated in Table 1. H₂O is set to be 15% for SR123,
 191 OF2512, and 10% for TRE 1 to ensure fluid saturation. Moreover, the bulk
 192 composition of sample TRE 1 is recalculated using individual mineral's modal
 193 percent and composition, because the originally provided bulk composition does not
 194 incorporate the garnet core (no MnO considered). In the TRE 1 sample, the MnO
 195 composition is effectively zero in the garnet rim but relatively high in the garnet core.
 196 Therefore, it is assumed here that half of the garnet radius is composed of the core
 197 composition and the other half has the rim composition to incorporate the MnO
 198 content included in the garnet core.

199 For sample SR123 (Russo *et al.*, 2006), the recalculated isochemical phase-diagram
 200 section is comparable to the original published one in Russo *et al.* (2006). The peak
 201 temperature for SR123 is slightly modified by 15°C by systematic testing of different
 202 peak temperatures to find the one that fits the garnet rim. The new phase-diagram
 203 section for sample OF2512 is similar for most of the phases, such as lawsonite, garnet,

204 coesite, omphacite and phengite. The biotite stability field is different. In the original
 205 phase diagram section, biotite is stable in the high pressure, low temperature and low
 206 pressure, higher temperature region whereas in the new calculation it is only restricted
 207 to low pressure (<20 kbar), and high temperature zone (< 650°C). This discrepancy is
 208 related to different default settings in the older release of the Perple_X package. One
 209 of the program option parameters called “site-check” was previously set to “false” as
 210 default to allow negative site fractions. In the new version, the default setting is site
 211 check “true” to reject unrealistic negative site fractions (see details in
 212 http://www.perplex.ethz.ch/perplex_options.html). For sample TRE 1, Ballevre *et al.*, (2003) computed the bulk composition by neglecting the garnet core that is rich in
 213 MnO in order to perform phase diagram section calculation. In our model, we
 214 compute the whole rock chemistry including garnet core to perform garnet growth
 215 model along a P - T path with fractionation. Therefore, the new phase diagram section
 216 is different from the MnO absent model in Ballevre *et al.*, (2003). The major
 217 difference is that garnet becomes stable in the entire isochemical phase-diagram
 218 section but the topologies of the other major phase fields remain the same. The
 219 chlorite stability field is extended to higher pressures and temperatures. The peak
 220 temperature for sample TRE 1 estimated by Ballevre *et al.* (2003) at 450°C lies in the
 221 lawsonite stability field. However, the calculated garnet zoning profiles for the newly
 222 derived bulk rock composition do not fit the measured profiles using this peak
 223 temperature. According to the new phase diagram section, garnet continues to grow
 224 along the clockwise P - T path suggested in Ballevre *et al.* (2003) beyond the lawsonite
 225 stability field. Therefore, the new peak temperature for sample TRE 1 deviates from
 226 450°C by 85°C to reach the composition of the garnet’s outermost rim by systematic
 227 testing of different peak temperatures. This temperature shift is also potentially
 228 induced by the aforementioned change in bulk chemistry as the uncertainty originated
 229 from the change of the bulk composition can be significant (Palin *et al.*, 2015).

231

232 **Results**

233 The calculated results for the three selected samples are illustrated in Figures 5, 6, 7.
 234 Only the total residual map slices (grossular + almandine + spessartine + pyrope) are
 235 portrayed as they represent the comprehensive fitting residual for all the four end
 236 members. The figure setup resembles the grid discretization shown in Figure 3a (note
 237 that the temperature coordinate is reversed to visualize the minimal error).

238 The residual map slices are arranged as (1) zero magnitude of pressure variation
 239 (isobaric); (2) the best fit magnitude of pressure variation, and (3) the doubled best fit
 240 magnitude of pressure variation (Fig. 5a, 6a, 7a). The best fit P – T path always lie in
 241 the middle slice with non-zero $Pvar$, indicating that an improvement of the quality of
 242 the P – T path can be achieved with the prescribed grain-scale pressure variation. The
 243 best fit P – T conditions are labeled on each residual map slices. The position of the
 244 best fit P – T conditions vary slightly as the magnitude of pressure variation changes.

245 The 2-D garnet element map using the best fit P – T – $Pvar$ conditions are calculated
 246 (Fig. 5d, 6d, 7d). The calculated profiles with the best-fit magnitude pressure
 247 variation (black lines) are illustrated individually and compared with the extracted
 248 measured profile (blue dots; Fig. 5d, 6d, 7d). The direction of the extracted profile is
 249 always parallel to the long axis of the grain, as it represents the highest asymmetry
 250 (see truncated horizontal profile A–B in Fig. 2). The calculated profiles assuming no
 251 pressure variation are characterized by the green dashed curves (Fig. 5d, 6d, 7d), to
 252 show the difference caused by pressure variation.

253 The best fit P – T – $Pvar$ conditions are tabulated in Table 1 for all the samples together
 254 with the calculated and the observed garnet volume percentage. Different samples
 255 reveal different magnitude of pressure variation depending on the asymmetry of the
 256 zoning profile and the bulk composition.

257

258 **DISCUSSIONS AND IMPLICATIONS**

259 The primary aim is to investigate the effect of grain-scale pressure variation on a

growing metamorphic mineral, taking garnet as an example. Results from the numerical model document that the effect of grain-scale pressure variation may be responsible for the development of the asymmetric chemical zoning. Asymmetrically zoned garnets are commonly observed in metamorphic rocks but are mostly measured along the chemically symmetric half of the profile or simply not considered. However, several models explaining the garnet asymmetry were proposed: 1) plastic deformation or brittle fracturing of garnet (Azor *et al.*, 1997; Storey & Prior, 2005; Kim, 2006; Terry & Heidelbach, 2006; Bestmann *et al.*, 2008; Floess & Baumgartner, 2013); 2) sluggish chemical diffusion in garnet (Wilbur & Ague, 2006; Carlson *et al.*, 2015); 3) garnet grains impingement and annealing (Whitney & Seaton, 2010); 4) heterogeneous chemical distribution around a growing garnet due to a limited mass transport in the matrix (O'Brien, 1999; Bruno & Rubbo, 2006). This scenario has been suggested to be likely considering the implication of sluggish chemical diffusion of rate controlling ion (Al^{3+}) in a corona structure (Carlson, 2010). If there is no observational evidence that any of the above mentioned models can be applied and when mass transport in the matrix and grain boundaries is fast, pressure variation may be a possible explanation for the asymmetric chemical zoning in garnet.

The constrained pressure variation provides an indication on how much the system pressure can deviate from the isobaric conditions to produce the asymmetric zoning assuming that asymmetric chemical zoning is entirely due to this pressure gradient. The simulations provide insight into the quality of the P - T path estimates and the role of the P - T increment during the garnet fractionation. The pressure variation amplitude can influence the relative position of garnet core and thus provide more realistic calculated zoning profile when compared to petrographic observations. Specific issues about the magnitude, effect and further implications of pressure variation, as well as the limitation of the numerical approach are discussed below.

286

287 **Implications for thermobarometric estimates**

288 The prescribed magnitude of pressure variation has an influence on the best fit P – T
 289 path for the asymmetrically zoned garnet. Such influence can be large, as in sample
 290 TRE 1 (9 kbar and 50 °C for the starting point; Fig. 7a), or small, as in sample SR123
 291 and OF2512 (about 1 kbar and 10 °C; Fig. 5a, 6a, respectively). Note that in sample
 292 TRE 1, two plausible P – T regions with low fitting residual are found for each
 293 magnitude of pressure variation (the red regions of low fitting residual in Figure 7a).
 294 One of the low residual regions, which has smaller residual at 0 kbar of pressure
 295 variation, vanishes as the magnitude of pressure variation increase, whereas the other
 296 low residual region gradually decreases in its residual and eventually provides the best
 297 fit P – T path (Fig. 7a). Without introducing pressure variation, the first low residual
 298 region will be accepted as the most plausible one. The validity of our garnet model is
 299 supported by the petrological observation in Ballevre *et al.* (2003) where amphibole
 300 and epidote inclusions are trapped in garnet grains as predicted from the P – T section
 301 along the P – T path involving the pressure variation (Fig. 4c). No amphibole or
 302 epidote is found along the P – T path if the magnitude of pressure variation is taken as
 303 zero (see Fig. 4c, 7). This suggests that the phases crossed along a linear P – T path
 304 simulated with pressure variation fits the actual observation better than the modelled
 305 ones without pressure variation.

306 The deviation in the P – T space caused by the pressure variation may be significant if
 307 the garnet is more asymmetric than the provided examples. When the pressure
 308 variation is higher, the equilibrium garnet volume fraction and end member
 309 proportion in each cell also vary which influences the best fit starting P – T conditions.
 310 Therefore, an improved starting P – T condition can be found with the prescribed
 311 pressure variation, assuming that other factors, such as sluggish kinetics, surface
 312 energy, local chemical equilibrium, do not significantly influence the garnet
 313 asymmetry.

314

315 **The sensitivity of modelling to the chosen P – T increment**

316 The asymmetry of garnet chemical zoning in the model is subject to the P – T
 317 increment along the P – T path as illustrated in Fig. 8. When the P – T path first hits the
 318 initial garnet entry isopleth, the garnet nucleus grows and the bulk composition is
 319 fractionated, causing the garnet entry boundary to migrate to higher P – T conditions.
 320 For the P – T conditions of the next increment on the path two extreme end members
 321 can be envisaged. (1) If we consider an extremely small P – T increment, for a fixed
 322 non-zero magnitude of pressure variation, only part of the garnet would touch the
 323 entry isopleth at the next equilibrium condition (Fig. 8b). In the applied model, this
 324 would predict large asymmetry even at small magnitude of pressure variation. (2)
 325 Contrarily, if we assumed a large P – T increment, more symmetrically shaped garnet
 326 would grow under the same magnitude of pressure variation because the pressure
 327 around the entire garnet would lie in the garnet stability field (Fig. 8c).

328 The model garnet asymmetry is quantified using the radius ratio which is defined as
 329 the ratio of the maximum and minimum distance to the core in a bilateral bisection
 330 through the grain (see the illustration of a zoned garnet profile in Fig. 9a). The radius
 331 ratio of the measured profile is set as an input, and serves to distinguish how
 332 asymmetric the garnet is. The radius ratio of the modeled zoning profiles is plotted as
 333 contours in Fig. 9, where the radius ratio of the measured garnet profile is represented
 334 by the thick black contour. The black contour represents the situation where the
 335 measured and the calculated zoning profiles match each other in terms of their
 336 geometrical asymmetry. This radius ratio of the modeled profiles can be kept constant
 337 while the magnitude of pressure variation and P – T increment is varied (see contours
 338 in Fig. 9).

339 Based on Fig. 9, the magnitude of pressure variation that gives the best fit converges
 340 to a small but non-zero value when the P – T increment is sufficiently small (high
 341 resolution in Fig. 9). For a T increment above 10–15°C, the required magnitude of
 342 pressure variation is large. An estimate of minimal 5°C T increment corresponds to a

343 magnitude of pressure variation ranging from 1.5 to 9 kbar depending on the specific
 344 sample as illustrated in Fig. 9. The choice of the P – T increment is partly constrained
 345 by the measured data because a sufficiently discretized P – T path is needed to obtain a
 346 reasonable fit. However, it may correspond to a range of possible pressure variations
 347 as shown in Fig. 9 (the blue low residual region), instead of a unique value. Thus, this
 348 examined range of the magnitude of pressure variation is geologically relevant if it
 349 provides a satisfactory fit between the measured and calculated garnet zoning profiles
 350 (i.e. if the lowest residuals in that range are acceptable). The best-fit magnitudes of
 351 pressure variation determined from Fig. 5–7 fall into this range, which represents the
 352 actual possible deviation from isobaric conditions that can be potentially used to
 353 interpret the metamorphic conditions.

354

355 **Pressure variation during prograde mineral growth**

356 The proposed model is applicable in the case where fluid pressure variation exists
 357 during growth of the fractionating mineral (i.e. garnet) along the prograde path. Below,
 358 three possibilities relevant to the presence of fluid pressure variations are discussed.

359 1) Hydrostatic fluid in a metamorphic reaction region

360 Etheridge *et al.* (1983) suggested that many low and medium metamorphic regions
 361 involve large-scale fluid circulations. This implies an interconnected porosity that
 362 allows porous flow to establish a hydrostatic fluid pressure gradient. The difference
 363 between the hydrostatic and lithostatic pressure gradient resulting from the density
 364 difference of fluid and solid and assuming no tectonic deformation implies that grain
 365 scale fluid pressure varies between lithostatic and hydrostatic pressure (see
 366 Introduction and Fig. 1). Although the fluid saturated grain boundaries have
 367 thicknesses on the nanometer scale, diffusion speed in such grain boundaries is
 368 sufficiently high to transport material efficiently around the grain (Gratier *et al.* 2013
 369 section 3.1 pp. 96). This is supported by pressure solution experiments in which the
 370 transport of dissolved material proceeds from the high fluid pressure in the thin film

371 to the low pressure side of the grain where it precipitates (De Boer *et al.*, 1977; Rutter,
372 1983).

373 2) Fluid saturated solids under stress

374 Under low permeability conditions, large-scale fluid circulations may be unlikely and
375 the pressure in the fluid may approach lithostatic pressure as summarized in Yardley
376 & Bodnar, 2014 (section 3.3 & 4.2 p. 86). However, heterogeneous solids under stress
377 generally give rise to heterogeneous stress and pressure distribution. Well understood
378 examples are spherical viscous inclusions undergoing shear in a higher- or lower
379 viscosity matrix (Schmid & Podladchikov 2003; Moulas *et al.*, 2014). More complex
380 microstructures and mineralogy lead to more heterogeneous stresses and the pressure
381 in this case does not necessarily show a simple and regular pattern (i.e. Wheeler, 1987,
382 Tajčmanová *et al.*, 2015).

383 The pressure of a fluid present at any time in the pores of the matrix or at grain
384 boundaries has to equal the local normal stress of the solid in order to maintain force
385 balance. Therefore, as long as the rock is under stress, fluid pressure variation
386 resulting from the force balance between fluid and solid is maintained. Therefore, the
387 magnitude and duration of fluid pressure variation is closely connected to stress levels
388 and relaxation of the solid. Depending on the viscosity of the matrix and the strain
389 rate, this may vary on the kbar level and be maintained on geological time scales
390 which has been documented by recent studies (Moulas *et al.*, 2014; Tajčmanová *et al.*,
391 2015, Dabrowski *et al.*, 2015)

392 3) Reactive transport

393 In a reactive system where a fluid phase is involved, fluid overpressure/ underpressure
394 can be generated by (de)–hydration reactions in compact metamorphic rocks
395 (Connolly, 1997). The fluid pressure evolution is mutually related to the speed of
396 metamorphic reactions. If fluid pressure locally generated by the reaction is faster
397 than the relaxation by flow, a significant pressure variation may develop during the
398 metamorphic reaction. Such a competition between devolatilization generated fluid

pressure and relaxation by flow has been studied thoroughly by Aarnes *et al.*, (2012). Moreover, several recent studies pointed out that the metamorphic reaction may occur over shorter duration than previously anticipated, from the order of 10 years to a few thousand years (Camacho *et al.*, 2005; Ague & Baxter, 2007; John *et al.*, 2012). Very rapid garnet growth up to c. 80 mm³ per thousand years is also measured using the Sm–Nd dating method that is potentially related to episodic fluid flow pulse (Pollington & Baxter, 2010). In the theoretical and numerical models on reactive transport and fluid flow (e.g. Steefel *et al.*, 2005), chemical reactions are considered to occur immediately during fluid flow. Therefore, a fluid pressure gradient must exist during the reaction in order to drive the fluid flow. Moreover, if the reaction rate is fast, it may provide enough time for mineral growth to record the pressure variations even if it grew in a mechanically dynamic and reactive environment.

411

412 **Model limitation and concluding remarks**

413 1. The P – T path is assumed to be linear. This is a first order approximation for the real
414 prograde P – T conditions. However, the real P – T path can be arbitrarily curved.
415 Similarly, the magnitude of pressure variation may also vary along the P – T path.

416 2. The magnitude of fluid pressure variation is assumed to be a constant. In nature, it
417 is not likely that the fluid pressure variation is maintained exactly the same over
418 geological time. The magnitude and spatial distribution of fluid pressure may be
419 subject to the chemical reaction, and mechanical environment around the garnet. It is
420 recognized that an increase of temperature in prograde metamorphism will reduce the
421 viscosity, thus further changes the pressure variation (see Fig. 1).

422 3. Fractionation of other phases may also need to be taken into consideration because
423 zoning has also been frequently observed in, e.g. plagioclase etc. This should be
424 carefully treated when other zoned minerals are observed in the sample.

425 4. Crystal size distribution (CSD; e.g. Higgins, 2000; Carlson, 2002; Ketcham &

426 Carlson, 2012) is not considered here due to a lack of CSD statistics in garnet zoning
427 literature. Only one garnet is assumed to grow in the given system, and it is equivalent
428 to multiple garnets model with same radius in terms of the shape of the chemical
429 zoning profile.

430 5. Diffusion in the fractionating crystal is not considered in the present model. The
431 model covers relatively low temperature region (below 600°C) where the influence of
432 diffusion is supposed to be minor as documented by other models (Ague & Baxter,
433 2007; Gaidies *et al.*, 2008 a, b; Caddick *et al.*, 2010).

434 6. The outcome of the model, estimated P – T path and magnitude of pressure variation
435 are subject to the choice of database and solid solution model. Careful consideration
436 must be made prior to the implementation of the thermodynamic model on the garnet
437 model discussed before.

438 7. Sluggish kinetics is not considered due to the assumption of complete equilibrium
439 in the matrix. The free variables in our model are pressure, temperature, and the
440 magnitude of pressure variation.

441 The model limitations, e.g. a linear P – T path, may potentially lead to mismatch
442 between the computed zoning profile and the measured ones, such as the opposite
443 polarity of the grossular zoning profile shown in Fig. 5d. Better match can be
444 achieved by adding more variations, such as P – T path curvature, crystal size
445 distribution, or even garnet absorption during a retrograde metamorphism after
446 prograde garnet growth. However, these additions would not generate any asymmetry
447 in the zoning. The purpose of this study is to provide an alternative to explain the
448 asymmetrically zoned garnet using only the local pressure variation. This may inspire
449 to reconsider the interpretation of the modeled P – T path determined by classical
450 petrology approaches and also to generally re-evaluate the asymmetrically zoned
451 minerals. The assumption of isobaric pressure around the garnet rim may potentially
452 lead to an inaccurately estimated P – T path. A consideration of the entire chemically
453 zoned profile provides not only a better estimate of P – T path but also an important

estimate of the magnitude of pressure variation on both side of the asymmetrically zoned garnet. Therefore, both quantification approaches – the classical isobaric and the polybaric alternative – may need to be equally considered in petrographic observations.

458

459 **ACKNOWLEDGEMENTS**

The authors address special thanks to Pierre Lanari, Mark Caddick, Roger Powell, and other two anonymous reviewers for their careful reviews and insightful suggestions that greatly improve the quality of the work. The authors sincerely thank Michael Brown for his editorial work. The authors are greatly indebted to Evangelos Moulas and Yuri Podladchikov for carefully reading the manuscript and providing valuable suggestions. The authors thank Taras Gerya and James Connolly for helpful discussions and critical questions on this model. Xin Zhong thank Julian Storck and Linwei Hu for providing feedback of the Introduction part. This work was supported by MADE-IN-EARTH ERC starting grant (n. 335577).

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- 663

664 **FIGURES AND TABLES**

665 **Table 1:** The model input data including solid solution models, P – T paths of the
 666 samples and model output including the best fit starting pressure, temperature,
 667 pressure variation, and calculated garnet mode. Sources of solid solution models are
 668 listed below the table.

Sample name No. of Fig. Reference	SR123 5 Russo (2006)	OF2512 6 Groppo (2009)	TRE 1 7 Ballevre (2003)
mineral solid solution phases	garnet, biotite, chlorite, feldspar, muscovite, cordierite, staurolite, amphibole	garnet, biotite, chlorite, feldspar, muscovite, omphacite, cordierite, amphibole, phengite	garnet, biotite, chlorite, feldspar, amphibole, omphacite, epidote
Peak P – T	10 kbar, 565°C	32 kbar, 600°C	18kbar, 535°C
P – T search domain	3~10 kbar 490~570°C	10~30 kbar 450~600°C	3~18 kbar 450~550°C
Best fit P – T point	3.6 kbar, 524 °C	9.3 kbar, 614°C	5.2 kbar 498°C
Best fit P var magnitude	1 kbar	0.75 kbar	0.75 kbar
Calculated Grt mode (vol%)	1.65 %	22.1%	16.5%
Observed Grt mode (vol%)	Not reported	Not reported	~15 %

669 The garnet, chlorite, chloritoid and staurolite solution models are from Holland &

670 Powell (1998); biotite model is from (Tajčmanová *et al.*, 2009); feldspar includes
671 plagioclase from (Newton *et al.*, 1980), and K-feldspar from (Thompson &
672 Waldraum 1968); amphibole model is from (Dale *et al.*, 2005); muscovite is from
673 (Coggon & Holland 2002).
674

675 **Fig. 1. (a)** Schematic curves showing an example of the trends for fluid pressure
 676 (denoted as P_f) in blue curve and lithostatic pressure (denoted as P_l considering
 677 both solid and fluid in a rock aggregate) in black line modified after Connolly, 2010
 678 and Connolly & Podladchikov, 2012. At depth, the fluid pressure first follows the
 679 lithostatic pressure gradient (proportional to the rock density ρ_r) above the reaction
 680 front. It is elevated at the reaction front due to devolatilization reactions. Within the
 681 porous reaction region, the fluid pressure drops following the hydrostatic gradient
 682 (proportional to fluid density ρ_f). Eventually the fluid pressure is elevated back to the
 683 lithostatic pressure at the bottom of reaction region where significant compaction
 684 occurs again. Therefore, the difference between fluid pressure and lithostatic pressure
 685 ΔP can vary in depth. **(b)** A zoomed-in grain-scale image at the depth indicated by
 686 the grey dash line assuming no tectonic deformation occurs. At this depth the fluid
 687 pressure is lower than the lithostatic pressure in (a). The depth scale is the same in (a)
 688 and (b). The width of grain-grain interface is exaggerated for illustration. The fluid
 689 pressure at the grain-grain interface (indicated by the black spot in (b)) has to be
 690 equal to the lithostatic pressure under no tectonic deformation (black spot in (a)) in
 691 order to maintain force balance in the direction perpendicular to the interface.
 692 Therefore, the pressure in open pores and at grain-grain interface are not equal to
 693 each other except at the depth where the fluid pressure and the lithostatic pressure
 694 overlap each other. At the depth of the grey dash line, the difference between the
 695 pressure in open pores and at grain-grain interface is ΔP characterized by the
 696 horizontal bracket in (a).

697 Fig. 2: (a) Local pressure variation as a function of orientation in degree. The pressure
 698 distribution is simplified as a sinusoidal function to capture the pressure variation. (b)
 699 A calculation using the pressure distribution shown in (a). The garnet starts to grow
 700 from a nuclei stage (I). The pressure is higher on the left and lower on the right side of
 701 the garnet. An asymmetrically zoned garnet is grown after the accumulation of a few
 702 shells. At stage (II), the compositional difference in one single shell can be observed
 703 due to the sensitivity of CaO to pressure. The outer shell of the asymmetric garnet is

704 already depleted in CaO. A horizontally truncated zoning profile can be plotted
 705 between point A and B representing the maximal zoning asymmetry in the last stage
 706 (III). Next to the image of stage (II), the magnified part illustrates the numerical
 707 structure of the growing garnet. **(c)** The P - T path and the pressure variation at
 708 different temperature points for illustration. The resolution along the P - T path must
 709 be set. In the present case, we choose to prescribe the lowest local pressure at the new
 710 P - T point to match the highest local pressure at the previous P - T point illustrated
 711 with the black horizontal dashed line. Detailed explorations and explanations on this
 712 setup is provided in Discussion. The P - T points along the path corresponds to the
 713 stages shown in (b).

714 **Fig. 3: (a)** Schematic P - T - $Pvar$ grids illustrating the approach defining the starting
 715 P - T - $Pvar$ point. Three coordinates represent temperature, pressure and the magnitude
 716 of pressure variation. For each starting P - T - $Pvar$ grid, a complete zoning profile can
 717 be calculated. The pressure variation constrained by dashed lines indicates the
 718 pressure range around the growing garnet. The width of the variation is defined by the
 719 amplitude of sinusoidal function in Fig. 1b. **(b)** An extreme case illustrating both the
 720 calculated (blue) and measured (red) profiles with different directions of higher
 721 pressure ends. In this case, the measured garnet profile (red) has higher pressure to the
 722 right (see red arrow), thus the distance from measured garnet core (peak concentration
 723 point) to the right rim is longer than the distance from garnet core to the left rim.
 724 Contrarily, the calculated profile (blue) has the opposite high pressure direction
 725 pointing leftward. Therefore, the distance from the garnet core to the right rim is
 726 shorter than the core to the left rim. This is because the amount of garnet in
 727 metamorphic rocks under equilibrium is often higher at higher pressure conditions.
 728 The short black arrows indicate the absolute distances between the measurements and
 729 the calculated profile. The residual for the calculated zoning profile can be acquired
 730 by averaging the distance between the calculated profile and the measured profile (the
 731 length of black arrows) through the entire zoning profile.

Fig. 4: Phase diagram section calculated using Perple_X for three samples. **(a)** SR123 (Russo *et al.*, 2006), **(b)** OF2512 (Groppo *et al.*, 2009), **(c)** TRE 1 (Ballevre *et al.*, 2003). The bulk compositions are given in wt%. The color shades indicate the garnet weight percent. The red curve is the garnet entry curve. In sample OF2512, and sample TRE 1, garnet is stable in the entire P – T space, suggesting that the garnet growth along the prograde P – T path start with a finite amount of garnet. The initial composition and weight percentage of the first shell of the garnet is computed at the starting point on the P – T path without considering the nucleation composition. The star represents the peak P – T conditions listed in **Table 1**. Mineral abbreviations follow Whitney & Evans (2010).

Fig. 5: **(a)** Total residual map sliced at isobaric condition ($Pvar=0$), best fit $Pvar$ at 1 kbar, and the doubled best fit $Pvar$ at 2 kbar. The stars indicate the peak P – T conditions. The pressure variations are illustrated within the white dash lines around the best fit P – T path. The lowest residual is indicated as black dot in the middle slice. Note the different best fit P – T conditions in the three slices. **(b)**, **(c)** The total residual as functions of temperature and pressure, respectively. The best fit temperature and pressure changes due to a change of pressure variation. **(d)** The calculated asymmetric garnet 2D element map and the extracted profiles compared to the measurements plotted with blue dots (Russo *et al.*, 2006). The garnet zoning maps and black profiles are calculated using the best fit P – T – $Pvar$ conditions denoted with the black dot in (a). The dash green profiles are calculated without the pressure variation following the P – T path shown in the left residual slice in (a). The profiles are in mole fraction unit.

Fig. 6: **(a)** Total residual map sliced at isobaric conditions ($Pvar=0$), best fit $Pvar$ at 0.75 kbar, and the doubled best fit $Pvar$ at 1.5 kbar. The stars indicate the peak P – T conditions. The pressure variations are illustrated within the white dash lines around the best fit P – T path. The lowest residual is indicated as black dot in the middle slice. Note the different best fit P – T conditions in the three slices. **(b)**, **(c)** The total residual as functions of temperature and pressure, respectively. The best fit temperature and

760 pressure changes due to a change of pressure variation. **(d)** The calculated asymmetric
 761 garnet 2D element map and the extracted profiles compared to the measurements
 762 plotted with blue dots (Groppo *et al.*, 2009). The garnet zoning maps and black
 763 profiles are calculated using the best fit P – T – $Pvar$ conditions denoted with the black
 764 dot in (a). The dash green profiles are calculated without the pressure variation
 765 following the P – T path shown in the left residual slice in (a). The profiles are in mole
 766 fraction unit.

767 **Fig. 7: (a)** Total residual map sliced at isobaric condition ($Pvar=0$), best fit $Pvar$ at
 768 0.75 kbar, and the doubled best fit $Pvar$ at 1.5 kbar. The stars indicate the peak P – T
 769 conditions. The pressure variations are illustrated within the white dash lines around
 770 the best fit P – T path. The lowest residual is indicated as black dot in the middle slice.
 771 Note the different best fit P – T conditions in the three slices. **(b)**, **(c)** The total residual
 772 as functions of temperature and pressure, respectively. The best fit temperature and
 773 pressure changes due to a change of pressure variation. **(d)** The calculated asymmetric
 774 garnet 2D element map and the extracted profiles compared to the measurements
 775 plotted with blue dots (Balleve *et al.*, 2003). The garnet zoning maps and black
 776 profiles are calculated using the best fit P – T – $Pvar$ conditions denoted with the black
 777 dot in (a). The dash green profiles are calculated without the pressure variation
 778 following the P – T path shown in the left residual slice in (a). The profiles are in mole
 779 fraction unit.

780 **Fig. 8:** Schematic diagram showing the influence of the equilibrium P – T increment on
 781 the asymmetry of garnet growth. The garnet starts to grow from a nucleus in **(a)** when
 782 the P – T conditions first touches the garnet entry isopleth. Fractionation leads to an
 783 increase of P – T conditions of the entry isopleth illustrated by the different color solid
 784 lines in **(b)**, **(c)**, and **(d)**. Three scenarios can be listed as **(b)** small P – T increment; **(c)**
 785 large P – T increment, and **(d)** medium P – T increment. Difference choices of P – T
 786 increment result in particular patterns of garnet shape and asymmetry shown in (b),

787 (c), and (d). The next shell's geometry can be varied depending on the position of next
 788 equilibrium P – T conditions.

789 **Fig. 9:** The influence of the magnitude of pressure variation v. P – T resolution
 790 (assigned as temperature increment on the top coordinate). The color indicates total
 791 residual of the calculated four end members. The contours are radius ratio of different
 792 values, among which the black ones are the measured garnet radius ratio. The white
 793 dashed lines indicate the position of 5°C temperature increment estimated as a
 794 minimal. The position where the contour of the measured radius ratio (black curve)
 795 and the estimated temperature increment cross indicates the corresponding magnitude
 796 of pressure variation required to grow the observed garnet geometry. Our predicted
 797 magnitude of pressure variations (0.75 to 1 kbar in Fig. 5~7) are generally below the
 798 pressure variation estimated at 5°C temperature increment (1.5 to 8.5 kbar).

799 **Fig. S1:** Benchmark comparison of our model with Theria_G (Gaidies *et al.*, 2008).
 800 The left images are calculated and presented using Theria_G software package. The
 801 crystal size here is the largest one, thus the zoning profiles represent the end member
 802 compositions along the entire P – T path. The right plots are calculated using our
 803 numerical approach with zero magnitude of pressure variation. Only half the profile is
 804 presented for comparison. Slight deviation on the core value (e.g. spessartine and
 805 almandine at the core position) might be related to the difference in solid solution or
 806 database. The P – T path and bulk composition are provided in Appendix S2. Profiles
 807 are illustrated in molar fraction.
 808

809 **APPENDIX S1**810 **Procedures of the forward model.**

811 The numerical model can be streamlined as following:

- 812 • Step 1: Start with a model composition that represents the whole rock
 813 chemistry; a P – T path experienced by the rock; and a magnitude of pressure
 814 variation around the garnet. Parameters such as the number of shell and cell
 815 are also set at the beginning. The above is all the parameters required for the
 816 numerical model.
- 817 • Step 2: Determine the P – T condition in each cell within the first shell as
 818 shown in Fig. 1b. The method used in our model is to simply apply a
 819 sinusoidal shaped pressure distribution as:

820
$$P_i = P + P_{var} \cdot \sin\left(\frac{2\pi}{n}i\right),$$

821 where P_i is the local pressure in cell i , P is the pressure located at the P – T
 822 path, P_{var} is the magnitude of pressure variation. The number of cell is
 823 assigned as n .

- 824 • Step 3: Use Perple_X to compute the equilibrium garnet modal percentage and
 825 garnet chemistry. The input information for Perple_X is the individual
 826 pressure within each cell (P_i), a common temperature, and a common effective
 827 bulk composition. The results are the equilibrium garnet weight percentage
 828 ($M_i^{\%}$), the volume percentage ($V_i^{\%}$), and the chemical composition ($X_i^{\%}$) in
 829 each cell i .
- 830 • Step 4: Assign the system mass to be M , and volume to be V . The garnet mass
 831 and volume of each cell M_i and V_i are computed by equally distributing the
 832 whole system to n cells:

833
$$M_i = \frac{M}{n} \cdot M_i^{\%},$$

834
$$V_i = \frac{V}{n} \cdot V_i^{\%}.$$

- 835 • Step 5: Convert V_i to radius in 2D model using the equation of sectorial area:

836
$$r_i^{new} = \sqrt{\frac{nV_i}{\pi} + (r_i^{old})^2},$$

in which the thickness of the 2D model is assumed as unity. r_i^{new} is the radius of the new garnet shell in cell i , r_i^{old} is the radius of the old garnet shell in cell i . If $i = 1$, r_i^{old} equals to zero. After the growth of the new layer, the system volume (V) will be updated by subtracting the newly formed garnet volume from the previous system volume.

- Step 6: Fractionate the bulk system composition. The mass conservation requires that:

$$\underbrace{(M - \sum_{i=1}^n M_i)X_{new}^{\%}}_{\substack{\text{the components mass} \\ \text{without garnet}}} = \underbrace{M \cdot X_{old}^{\%}}_{\substack{\text{the components mass} \\ \text{of the whole system}}} - \underbrace{\sum_{i=1}^n X_i^{\%} \cdot M_i}_{\substack{\text{the components mass} \\ \text{of the fractionated garnet}}}.$$

Upon rearrangement, we have:

$$X_{new}^{\%} = \frac{M}{M - \sum_{i=1}^n M_i} \cdot X_{old}^{\%} - \frac{\sum_{i=1}^n X_i^{\%} \cdot M_i}{M - \sum_{i=1}^n M_i},$$

where $X_{new}^{\%}$ is the new system chemical composition in mass percentage, $X_{old}^{\%}$ is the old system chemical composition in mass percentage. $X_{new}^{\%}$ must be normalized for the next round of calculation. After fractionation, the system mass (M) will be updated by subtracting the newly formed garnet mass from the previous system mass. The above equation is slightly different from the classical fractionation model in that the mass of the garnet shell is a sum of mass in all the cells, rather than one uniform value computed in one shell without pressure variation. In case of no pressure variation, the equations can be simplified by neglecting the “sum” signs and changing individual cell’s mass M_i into the mass of one entire shell.

- Step 7: Record the computed r_i^{new} , and chemical composition $X_i^{\%}$ in each cell, and return to Step 2 using the new P – T point and the fractionated bulk compositions in Step 6. Repeat the same calculation and record the radius and the composition of garnet at different cell along the P – T path. If the peak P – T point is reached, finish the code.

The final chemical zoning pattern can be plotted using the radius and the composition of the garnet in different cell and shell, which are recorded in Step 7. The initial rock mass (M) and volume (V) will not influence the shape of the

865 zoning pattern, but will influence the size of the grown garnet. The corresponding
866 radius can be normalized to the measured garnet radius for comparison purpose.
867

868 **APPENDIX S2**

869 **Benchmark of the forward model**

870 To benchmark our forward model, we use the same P – T path and bulk composition as
871 in Gaidies *et al.* (2008) to calculate garnet zoning profile without pressure variation
872 and compare half of the entire profile with the one calculated using Theria_G. The
873 result of benchmarking is illustrated in Figure S1 for all the four end members without
874 diffusion.

875 Differences arise because in our model volume percentage calculated from Perple_X
876 is converted into 2–D trapezoid area in each cell (equivalent to circle when cell
877 number is high enough as illustrated in Figure S1) while in Theria_G the volume
878 percentage is converted to radius in 3–D sphere. This will lead to a difference,
879 especially when the garnet grows larger. However, the results are still comparable in
880 terms of the value range and the shape of the calculated end member molar fraction
881 profile (Fig. S1).

882 The P – T path and bulk composition are the same as the Loop B in table 3 (Gaidies *et*
883 *al.*, 2008) and are provided in the table below. The model system is MnNCFMASH
884 and solid solutions are garnet and staurolite (Holland & Powell, 1998); plagioclase
885 (Newton *et al.*, 1980); biotite (Tajčmanová *et al.*, 2009); phengite as described at
886 (<http://www.esc.cam.ac.uk/astaff/holland/ds5/muscovites/mu.html>). Chlorite extended
887 from (Holland & Powell, 1998).

888 Table S1: the bulk composition of the benchmark model.

	SiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	H2O
wt%	59.77	16.57	5.87	0.07	2.62	2.17	1.73	3.53	15

889

890 Table S2: the P – T path of the benchmark model.

Node	$T(^{\circ}\text{C})$	$P(\text{bar})$
1	446.18	3345.11
2	523.58	6935.51
3	560.04	9270.83
4	567.55	9739.58
5	577.10	10062.50
6	588.03	10145.83
7	601.33	9968.75
8	607.14	9625.00
9	610.10	9229.17
10	606.78	8781.25
11	598.26	8250.00
12	551.91	5687.51
13	454.81	3210.71

891

Zhong *et al.*, Fig. 1

(a) Local pressure variation

(b) CaO Composition

(c) P - T path Zhong *et al.*, Fig. 2

Zhong *et al.*, Fig. 3

Zhong *et al.*, Fig. 4

Zhong *et al.*, Fig. 5

Zhong *et al.*, Fig. 6

Zhong *et al.*, Fig. 7

Zhong *et al.*, Fig. 8

Zhong *et al.*, Fig. 9

Zhong *et al.*, Fig. S1